

# U.S. Army Research Laboratory

SUMMER RESEARCH TECHNICAL REPORT

## **Growth and Transfer of Graphene for Device Fabrication**

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## Abstract

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The unique electronic properties of graphene enable the development of field effect transistors with potential for speeds much higher than the existing technology. Diluted methane chemical vapor deposition growth of graphene on a nickel substrate has resulted in potentially useful multilayer graphene layers. These graphene layers were grown on nickel substrates deposited onto silicon (Si)/silicon dioxide (SiO<sub>2</sub>) wafers by evaporation and sputter methods. The graphene must be transferred from the nickel substrate onto a template more suitable for device fabrication. However, the current graphene transfer process is not fully mature and presents a number of challenges. In the transfer process, a polymer coating is applied to the graphene, and the original materials underneath are removed. A coating of photoresist is spun and hardened on top of the graphene, and then the substrate is removed with a buffered oxide etch and a nickel etch. One challenge is removal of the photoresist from the surface of the graphene without film wrinkles, cracks, and contamination. Alternative solutions that minimize damage to the graphene during the transfer process are currently being explored.

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## Acknowledgments

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Special thanks go to Eugene Zakar, Barbara Nichols, and Greg Meissner for guiding my research.

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## **Student Bio**

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I am currently in my first year as a Student Temporary Employment Program (STEP) student at the U.S. Army Research Laboratory (ARL) in Adelphi, MD. I will be entering my second year as an undergraduate in Materials Science and Engineering at the University of Maryland this fall. My research at ARL has involved processing work within the cleanroom (sputtering, etching, and characterization) and optimization of the graphene growth and transfer processes. I plan on continuing my work at ARL in the future to fully optimize these processes and develop skills to characterize graphene using different methods.

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## 1. Introduction/Background

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Graphene, an atomically thick layer of carbon, has recently emerged as a material with the potential to greatly improve semiconductor devices. The zero bandgap width of graphene enables high electron and hole concentrations, which gives a high field effect mobility of about  $10,000 \text{ cm}^2/\text{Vs}$  (1). While graphene is most commonly referred to as a single layer, bilayer and multilayer graphene up to about 10 layers in thickness exhibit graphene-like properties; 10 or more layers tend to exhibit bulk graphite characteristics (2). Bilayer graphene is unique because it can form a bandgap between the two atomically thin layers (3). Large sheets of single layer graphene have already been produced through exfoliation methods (4), but the exfoliation process is limited. Exfoliation involves cleaving graphene from bulk graphite a single atomic layer at a time, which limits production to single-layer graphene. Additionally, the film produced is not uniform because it conforms to the roughness of the graphite sample being cleaved.

However, the growth of graphene using atmospheric pressure chemical vapor deposition (APCVD) is promising. APCVD graphene growth involves flowing diluted methane gas over a nickel sample in an isolated environment at about  $1000^\circ\text{C}$ . The nickel samples are either sputtered or evaporated onto silicon (Si)/silicon dioxide ( $\text{SiO}_2$ ) wafers. Nickel is an ideal substrate for graphene growth because it is approximately 0.9% with carbon (5), which causes the nickel to form a solution with the carbon it is exposed to from the diluted methane gas. When this solution is cooled at a controlled rate, the carbon segregates itself from the nickel substrate and forms a layer of graphene on the surface of the nickel. The challenges presented in APCVD graphene growth are optimizing the process to limit the number of graphene layers grown and minimizing defects and pitting caused by hydrogen gas exposed to the sample. The goal is to work toward a process that gives consistent smooth areas of bilayer graphene.

Before this graphene can be used for device fabrication, it is necessary to transfer the graphene onto a substrate with insulator properties. The current transfer process is still preliminary and presents a number of challenges. Since the process is a manual wet etch of the nickel substrate the graphene was grown on, the graphene can easily become contaminated, wrinkled, or torn. The process is currently being optimized to produce the best possible quality graphene.

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## 2. Experiment

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### 2.1 Graphene Growth

The graphene growth process (figure 1) requires the nickel substrate to be in an isolated environment at atmospheric pressure. Once isolated, the system is heated to about  $1000^\circ\text{C}$



while exposed to argon (Ar) and hydrogen ( $H_2$ ) gas. The argon acts as a carrier gas, while the hydrogen prevents oxidation of the nickel at high temperature. Once the system is ramped to temperature, the sample is annealed while exposed to argon and hydrogen. After the anneal period, methane gas ( $CH_4$ ) is introduced into the system and temperature is held for about 10 min while the carbon forms a solution with the nickel substrate. After this growth period, the system is ramped down to room temperature at a rate of  $5\text{ }^\circ\text{C/min}$ , which allows the carbon to segregate from the nickel sample and form graphene on top of the nickel.

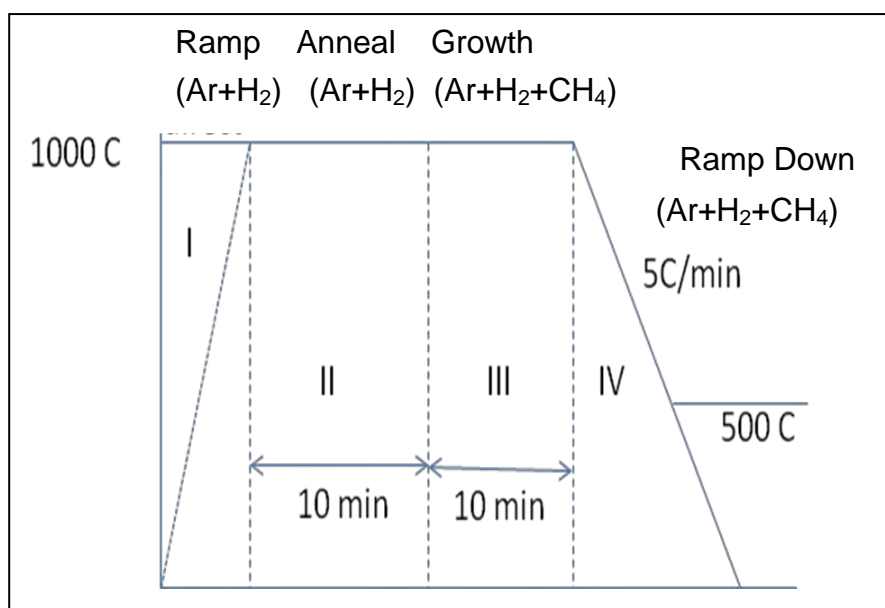


Figure 1. The graphene growth process involves the following: I. Ramp up phase to  $1000\text{ }^\circ\text{C}$  with Ar and  $H_2$  gases; II. Anneal phase with Ar and  $H_2$  gases for grain growth; III. Growth phase, where  $CH_4$  is introduced into the system; and IV. Ramp Down phase at  $5\text{ }^\circ\text{C/min}$  with continued exposure to Ar,  $H_2$ , and  $CH_4$ .

In order to control the number of graphene layers grown on the sample, the methane content was adjusted in search of an optimum value. Graphene was grown at  $975\text{ }^\circ\text{C}$  with the gas content held at 800 sccm Ar and 200 sccm  $H_2$  and a  $5\text{ }^\circ\text{C/min}$  ramp down. Four different runs were performed with the previous conditions held constant, but with varying methane content ranging from 5 to 2 sccm. In order to find conditions for graphene growth that minimized defects from hydrogen, graphene was grown in a series of experiments that used ranges of hydrogen from 300 to 700 sccm. Growth was also attempted at temperatures ranging from 975 to 900 to  $800\text{ }^\circ\text{C}$ .

## 2.2 Graphene Transfer

Once graphene suitable for device fabrication is produced, the graphene is transferred onto a substrate suitable for device fabrication by a wet etch process (figure 2). First, a layer of poly(methyl methacrylate) (PMMA) is manually spun on the surface of the nickel-graphene sample to protect the graphene layer. After the PMMA is spun on the surface, the sample is floated in a BOE for 1 h and rinsed. The sample is then floated in a nickel etchant until the

nickel layer is visibly removed. After a float rinse in water, a new oxidized Si substrate is used to scoop the layer of graphene and PMMA out of the water. This substrate was used because graphene is visible on the surface of SiO<sub>2</sub>. After baking the graphene onto the Si/SiO<sub>2</sub> substrate, an acetone vaporization method was used to removed the PMMA from the graphene's surface. By heating acetone to 110 °C and submerging the sample in the acetone four separate times, a clean graphene sample on SiO<sub>2</sub> is obtained.

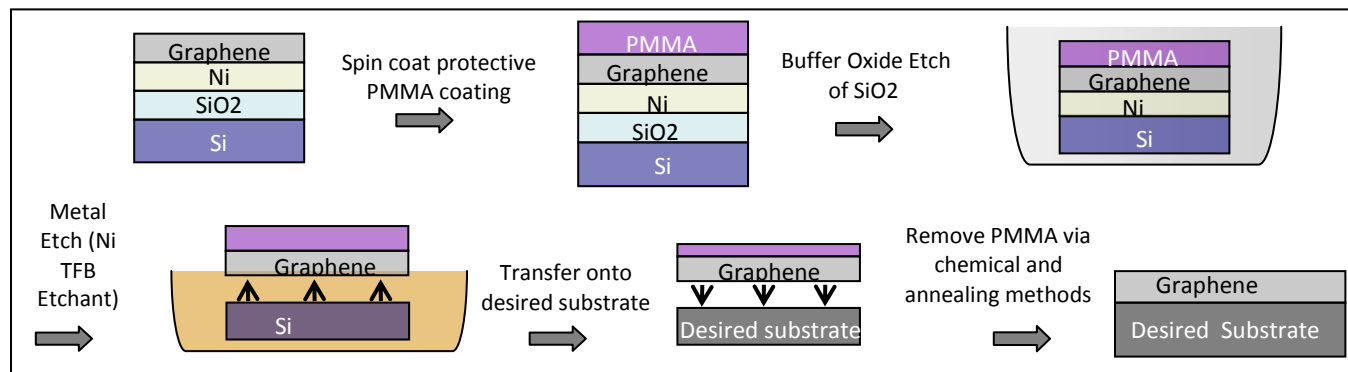


Figure 2. The graphene transfer process off a nickel-based substrate involves undercut etching of the SiO<sub>2</sub> layer, then of the nickel layer to float the graphene off the surface of the substrate. The new substrate of choice is then used to manually scoop the graphene film onto its surface.

### 3. Results and Discussion

#### 3.1 Graphene Growth

When graphene was grown at different ranges of methane content from 0.5% to 0.2%, it was found that decreased methane content caused less graphene to grow (figure 3). GPH100, the sample grown with 0.3% methane content, was tested using Raman spectroscopy to characterize the approximate number of layers in the sample (figure 4). It was found that darker patches on the sample surface were found to be thick multilayer graphene, lighter patches were approximated to be about five layers, and transparent spots were few layers or potentially bilayer (table 1). Since as methane content was decreased, graphene samples displayed few dark and light patches and more consistently smooth transparent patches, the interpretation of the Raman spectroscopy data shows as methane content was decreased, multilayer graphene patches also decreased and larger areas of smooth few-layer graphene increased.

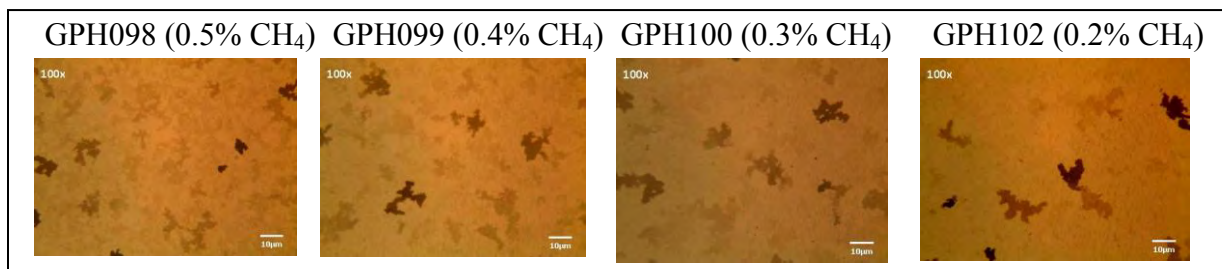


Figure 3. Graphene samples were grown at 975 °C with 800 sccm Ar and 200 sccm H<sub>2</sub> gas flows and 5 °C/min ramp down. The methane content was decreased, and smoother graphene with fewer multilayer patches was grown as methane decreased.

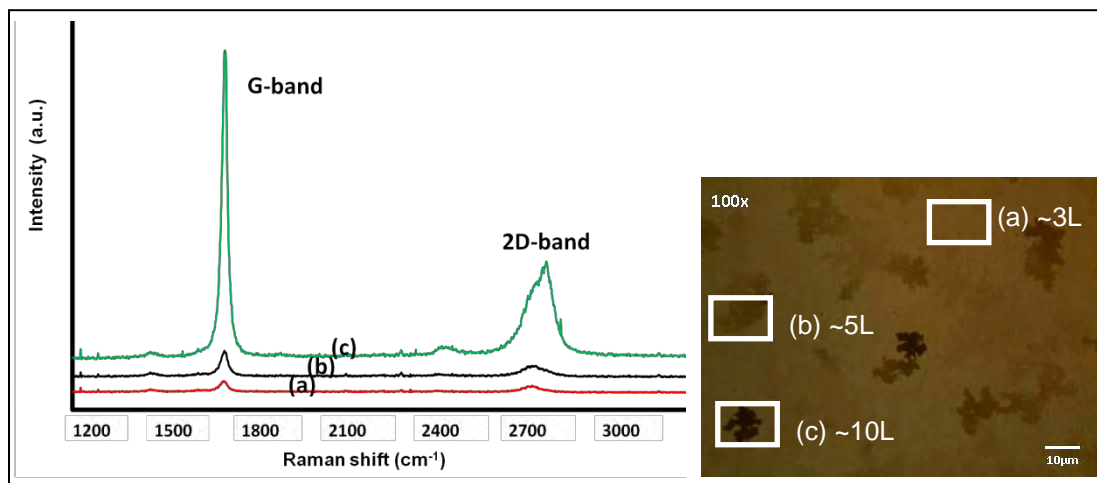


Figure 4. Raman spectroscopy data peaks correspond to spots tested. Higher intensity peaks occurred at points where there were darker patches of graphene. (Data provided by Center for Advanced Material Characterization at the University of Oregon.)

Table 1. Interpretation of Raman spectroscopy data approximates the number of graphene layers on a nickel sample (6).

Raman Spectroscopy Data Interpretation		
Ratio (G/2D)	Graphene Layers	2-D Peak
<0.5	Single Layer	Sharp
~1	Bi-Layer	Broad
~3	3 Layers	Broad
~5	Multi-Layer	Broad

When testing growth with differing ranges of hydrogen, it was found that as the hydrogen content increased at temperatures of ~1000 °C, the defects increased in number and became larger. However, it was found that at decreased temperature more hydrogen could be used without causing defects to the nickel surface. At 900 °C, 400 sccm of hydrogen was effectively used to aid in graphene growth, while this same flow of hydrogen caused defects at 975 °C. By lowering the temperature at which graphene growth takes place, hydrogen defects were successfully eliminated.

### 3.2 Graphene Transfer

By following the previous graphene transfer process, graphene was successfully transferred onto a Si/SiO<sub>2</sub> substrate (figure 5). However, the process is still preliminary and presented a number of difficulties. Since the PMMA is spun on manually, it actually attaches to the sides of the sample and prevents the buffered oxide etchant from removing the SiO<sub>2</sub> layer. This problem was combated by manually cleaving the PMMA from the sides of the sample with a razor, and then using acetone to clean the sides of the sample. This helped the BOE etch more quickly, but also caused tears in the sides of the graphene.

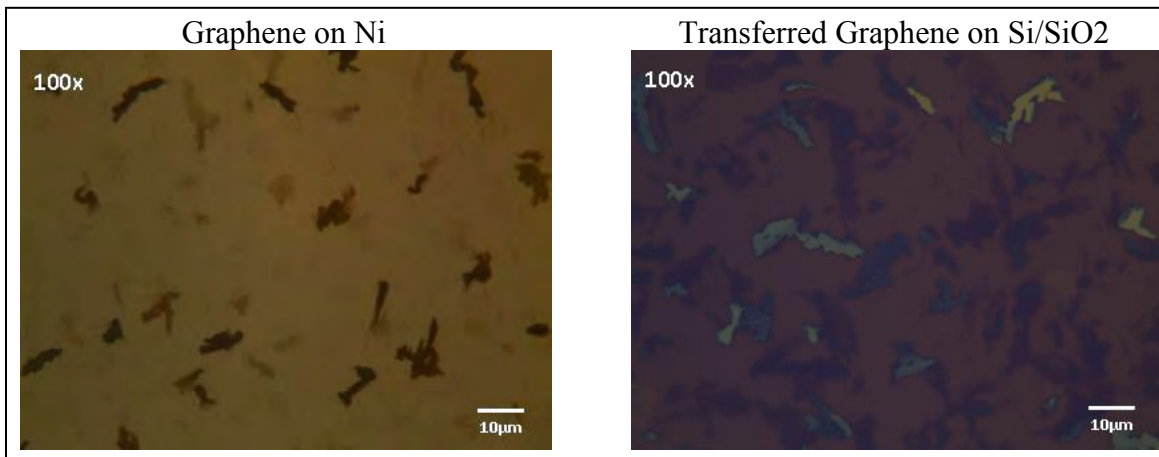


Figure 5. Graphene is pictured before and after transfer from the nickel-based substrate of grown to an oxidized silicon substrate. SiO<sub>2</sub> is an ideal substrate because of its insulator properties and because graphene is visible on its surface.

The BOE was able to etch part of the SiO<sub>2</sub> layer, but it was not particularly effective because the nickel etchant took multiple days to completely release the graphene from the surface of the nickel. Even when the nickel was completely etched, the graphene was still partially attached to the surface of the substrate it was grown on and had to be removed with a razor. Although the graphene was successfully transferred onto the Si/SiO<sub>2</sub> substrate, the process was not completely optimized to prevent damage to the graphene.

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## 4. Summary and Conclusions

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By varying the methane and hydrogen content in a series of graphene growth experiments, optimum conditions for temperature and methane and hydrogen content were found. By reducing the methane to the lowest possible content at which growth still occurs and lowering the temperature to 900 °C to eliminate hydrogen pitting, larger areas of smooth few-layer graphene was grown with fewer defects. Graphene samples grown at 900 °C with 0.3% methane content exhibited surfaces suitable for nanoscale devices. More work must be done to continue

to optimize different variables in the growth process and further reduce the number of layers grown, with bilayer graphene being the goal.

In order to optimize the transfer process, it is important to find a successful etchant for the SiO<sub>2</sub> layer of the nickel-graphene substrate. Since the PMMA on the sides of the sample, even when manually cleaved, seemed to hinder the BOE from etching, future plans for optimizing the graphene transfer process involved the use of a different etchant for the SiO<sub>2</sub> layer. Once the SiO<sub>2</sub> layer can be successfully etched, the nickel etchant will be able to fully remove the nickel layer so the graphene can lift off the surface and enable transfer that minimizes tears and defects in the graphene. Future efforts will include the use of a 49% HF solution and HF vaporization to attempt to better etch the SiO<sub>2</sub> layer.

Graphene's advantages in electrical mobility and its unique electronic properties show promise for eventual industrial-scale device production. In order to reach the ability to mass produce graphene devices, it is important to create a process that is easily executable and produces quality results. Through the optimization of temperature and gas content in the growth of graphene and the successful transfer of graphene onto a Si/SiO<sub>2</sub> substrate, the process of APCVD graphene production has evolved to give graphene with fewer layers and better quality. By finding graphene layers can be reduced through controlling methane content, this process can be applied with optimized hydrogen flow and temperature to form nickel-grown graphene with the fewest layers possible. Through successful transfer of this graphene, device fabrication becomes practical with few-layer graphene grown on a nickel substrate.

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